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Greywater irrigation as a source of organic micro-pollutants to shallow groundwater and nearby surface water.

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Abstract

Increased water demands due to population growth and increased urbanisation have driven adoption of various water reuse practices. The irrigation of greywater (water from all household uses, except toilets) has been proposed as one potential sustainable practice. Research has clearly identified environmental harm from the presence of micro-pollutants in soils, groundwater and surface water. Greywater contains a range of micro pollutants yet very little is known about their potential environmental fate when greywater is irrigated to soil.

Therefore, this study assessed whether organic micro-pollutants in irrigated greywater were transferred to shallow groundwater and an adjacent surface waterway. A total of 22 organic micro-pollutants were detected in greywater. Six of these (acesulfame, caffeine, DEET, paracetamol, salicylic acid and triclosan) were selected as potential tracers of greywater contamination. Three of these chemicals (acesulfame, caffeine, DEET) were detected in the groundwater, while salicylic acid was also detected in adjacent surface water. Caffeine and DEET in surface water were directly attributable to greywater irrigation. Thus the practice of greywater irrigation can act as a source of organic micro-pollutants to shallow groundwater and nearby surface water. The full list of micro-pollutants that could be introduced via greywater and the risk they pose to aquatic ecosystems is not yet known.

1. Introduction

Greywater reuse has been internationally adopted as a mechanism to ease water demand pressures (Eriksson et al., 2002; Winward et al., 2008; Eriksson and Donner, 2009; Maimon et al., 2010; Turner et al., 2013; Zhu et al., 2015; Turner et al.; 2016). Although greywater is a suitable water reuse mechanism, greywater can contain numerous pollutants ranging from large concentrations e.g. phosphorus (245 mg L^{-1}) and sodium (1852 mg L^{-1}) (Travis et al., 2010; Stevens et al., 2011; Mohamed et al., 2013; Turner et al., 2013; Albalawneh et al., 2016) to below 1 µg L^{-1} for some metals and organic micro-pollutants (Eriksson and Donner, 2009; Donner et al., 2010; Turner et al., 2016). Due to the presence of numerous chemicals in greywater, the sustainability of greywater irrigation to soil has been questioned (e.g., Stevens et al., 2011; Turner et al., 2013; Turner et al; 2016). This work focussed on contamination of soils by nutrients, cations and anions. However, there has been minimal research into the presence, fate and effects of organic micro-pollutants in greywater (Eriksson et al., 2002; Eriksson et al., 2009; Donner et al., 2009, 2010; Hernández-Leal et al., 2011; Revitt et al., 2011; Murillo-Torres et al., 2012). Organic micro-pollutants are emerging as compounds of concern worldwide (Barceló, 2012) and very few long term studies have assessed emerging organic contaminants. Although these compounds are found in very low concentrations they can still affect the environment (Santos et al., 2010; Murillo-Torres et al., 2012; Gulyas et al., 2013). For example, triclosan is an antimicrobial agent used extensively in personal care products (Tamura et al., 2013); it is commonly detected in the aquatic environment (Gao et al., 2013, Montaseri and Forbes, 2016) due to its poor removal in wastewater treatment process. Triclosan is highly toxic to algae and can impact the reproduction and development in some fish species (Orvos et al., 2002; Dann

and Hontela, 2011). Another organic micro-pollutant, N,N-diethyl-m-toluamide (DEET, a personal care product used in insect repellents), is potentially persistent in the environment although the available data are contradictory. Cordy et al. (2004) showed that there were minimal DEET concentration changes in a soil column experiment after 23 days. Whereas Weeks et al. (2010) stated that DEET half-life was days to weeks and was not persistent and does not bio-accumulate.

Greywater contains numerous micro-pollutants (such as triclosan and DEET) (Eriksson et al. 2002 and 2009; Donner et al. 2010; Hernández-Leal et al. 2011, Revitt et al. 2011). However the environmental hazard of micro-pollutants in greywater irrigated on soil (Travis et al., 2010; Turner et al., 2016), surface water and groundwater (van Wezel and Jager, 2002; Eriksson et al., 2009) are not as well established and understanding the potential transport pathways are both important to addressing potential environmental contamination issues. The range of micro-pollutants found in greywater is extensive (Eriksson et al., 2002) and the interactions of these compounds (in-situ interaction within greywater holding tanks) and creation of other compounds through this interaction is relatively unknown. However, Hernández-Leal et al. (2011) did identify that ozonation and activated carbon adsorption had the capacity to remove greater than 99% of organic micro-pollutants in aerobically treated greywater. It is therefore assumed that the majority of organic micro-pollutants can be treated and that the impacts should be minimal if appropriate treatment systems are used for greywater reuse. Unfortunately much irrigated greywater receives limited or no treatment and thus has the potential to deliver organic micro-pollutants to the environment.

The aim of this study was to determine if the practice of greywater irrigation to soil can lead to contamination of groundwater and adjacent surface waterways by organic micro-pollutants. To do this greywater from a household with a greywater system was sampled over seven days, organic micro-pollutants in the greywater were identified and quantified and then groundwater and surface water from an adjacent waterway were analysed for a subset of the detected micro-pollutants.

2. Methods

Study area

The study site is located approximately 10 km west of Brisbane, Australia and is at the base of a High Ecological Value (HEV) [1] area of the Enoggera Reservoir catchment (EHP, 2010). The study site consists of a residential sub-division of 22 household lots that border 200 m of Enoggera Creek (Figure 1). All households have a greywater irrigation system. Each lot has a 200 m^2 grassed transpiration zone to receive the greywater irrigation. The water supply for each household is captured rain water that is stored in rainwater tanks and can be supplemented by council potable water. One lot (lot D) was chosen for this study (Figure 1). The site was selected based on previous research by Turner et al. (2013 and 2016) which showed that the household produced an average volume of greywater with moderate concentrations of pollutants in the irrigated greywater and thus can be considered as representative of sites in this residential development. This particular lot is also at the base of a hill and is located closest to Enoggera Creek with a line of sight distance of ~98m (Figure 1).

Figure 1

Greywater sampling and analysis

The greywater is treated (vermiculture) and stored onsite in a concrete greywater treatment system (Biolytix, 2005) and subsurface drip irrigated onto a 200 m^2 transpiration zone. Greywater consisted of all water discharged from the bathrooms, laundry and kitchen apart from blackwater (toilet waste). Daily sub-samples of greywater were taken each day over seven days between 24th to 30th March 2014, with a duplicate sample taken on day 4 (eight samples in total). Each greywater sample was taken directly from the irrigation outlet by forcing the irrigation cycle and sub-sampling the stream via a capillary tube. This sub-sample potentially represented up to 24hrs of stored greywater in the treatment system (maximum storage volume 1600L per day (Biolytix, 2005)). Samples were collected in 1 L amber glass solvent rinsed bottles, stored in an insulated container on ice and sent to the laboratory. A signal greywater sample was initially sent to the Queensland

[1]Under the Queensland Environmental Protection Act 1994, the Environmental Protection (Water) Policy 2009 (EPP Water) provides the framework for developing environmental values, management goals and water quality objectives for Queensland waters. For aquatic ecosystem environmental values, the EPP Water identifies four levels of protection according to the current condition of waters. These are high ecological value (HEV), slightly disturbed, moderately disturbed and highly disturbed. For HEV waters, the management intent is to maintain natural values/condition, and water quality objectives are set accordingly to maintain this natural state (Department of Environment and Heritage Protection, 2016).

Health Forensic Scientific Services (QHFSS) organic chemical laboratory to scan for 252 different organic micro-pollutants (Supplementary Information – organic micro-pollutant quality assurance and quality control) and were analysed by a high performance liquid chromatography mass spectrometry (HPLC - MS) using the method based on US EPA., Method 1694 (2007). Once initial screening was done, eight greywater samples were then sent to the National Research Centre for Environmental Toxicology (Entox), University of Queensland for routine analysis of greywater to a smaller subset of compounds, based on the results of the screening process discussed later. Greywater samples were filtered with 0.2 µm regenerated cellulose syringe filters (Phenomenex, Lane Cove, Australia) then spiked with deuterated standards (to have a final concentration of 1 µg L^{-1}) before analysis. The samples were analysed using a slightly modified version of the method of O'Brien et al. (2014). In summary, the analysis was performed using a Sciex QTrap 5500 (Sciex, Concord, Ontario, Canada) with electrospray ionization (ESI) interface coupled to a Shimadzu Nexera HPLC systems (Shimadzu Corp., Kyoto, Japan). Separation was achieved on a Kinetex Biphenyl column using a mobile phase gradient of 1 to 95% methanol with 0.1% acetic acid. The QTrap 5500 was operated in scheduled multiple reaction monitoring mode, with a 50 µl sample injection volume. Calibration standards ranged from 5 ng L^{-1} to 1 µg L^{-1}. For analytical detection limits, field blanks and duplicate samples see Supplementary Information – organic micro-pollutant quality assurance and quality control. A subset of six of the micro-pollutants detected in greywater (i.e., acesulfame, caffeine, DEET, paracetamol, salicylic acid and triclosan; the reason for this subset is explained in results and discussion section) were then analysed for in groundwater and surface water.

Groundwater sampling and analysis

Three piezometers were installed in a gradient transect behind the selected lot (Figure 1) towards Enoggera Creek. This transect was designed to capture any off-site transport of organic micro-pollutants via the groundwater as a result of greywater irrigation and to identify organic micro-pollutants that may subsequently be transported towards Enoggera Creek. Figure 1 identifies each individual piezometer and the general slope of the area. In general, perched groundwater direction and flow, will follow topography (Apgar, 2000), and in general will then potentially flow to a waterway.

The installation of the piezometers was conducted by a qualified and licensed driller operating a Geoprobe 6600 series drilling rig following the procedures set out in the "Groundwater Sampling and Analysis – A Field Guide. Geoscience Australia" (Sundaram, 2009) and adhering to the *Water Act 2000* (Queensland, 2015). Each piezometer had an approximate depth of 3.0 m. Groundwater samples were collected between November

2013 and April 2014. Groundwater samples were collected from the piezometers with a low flow peristaltic pump. Sampling from the piezometers was conducted in accordance with the Australian Standard: AS/NZS 5667.1:1998 (Standards Australia, 1998a; 1998b). Groundwater samples were collected in 1 L amber glass solvent rinsed bottles, stored in an insulated container on ice and delivered to the laboratory. Groundwater samples were analysed in the same manner as greywater samples.

Surface water sampling and analysis

Enoggera Creek was sampled to determine concentrations of organic micro-pollutants and to assess the fate of organic micro-pollutants as a result of greywater irrigation. Three sites were selected: a control site (upstream of potential groundwater inputs affected by the greywater irrigation), an impact site (downstream of potential groundwater inputs affected by the greywater irrigation) and a reference site located in the Enoggera Reservoir as this was the source water for Enoggera Creek (Figure 1). The distance between the reservoir wall and impact site is approximately 340 m in stream length and the impact site is approximately 200 m further downstream (Figure 1). The majority of surface runoff and groundwater will originate from the subdivision in this 200 m section of the creek (Figure 1). Ambient water quality sampling of Enoggera Creek occurred monthly between September 2013 and June 2014, and there was an increased frequency of sampling under high flow conditions during November 2013 and May 2014. Surface water samples were collected in 1 L amber glass solvent rinsed bottles using a sampling pole, stored in an insulated container on ice and delivered to the laboratory. Surface water samples were analysed in the same manner as greywater and groundwater samples.

Statistical analysis

Statistical analysis was preformed using XLSTAT, version 2014.4.02. Summary statistics (mean, standard deviation, maximum and minimum) were calculated for all data. Organic micro-pollutant concentrations for the surface water were natural log transformed to normalise their distribution prior to testing by analysis of variance (ANOVA). ANOVA in conjunction with Bonferroni analysis was used to assess if there were statistically significant ($P \leq 0.05$) differences between the Enoggera Creek sites (Impact, Control and Reference sites). The Bonferroni analysis is generally used for multiple comparisons between water quality sampling sites (Sargaonkar et al., 2008; Le et al., 2013) to minimise Type I statistical errors in rejecting the null hypothesis where a false positive occurs.

Calculation of the concentration of micro-pollutants potentially available for transport to aquatic environments

The organic micro-pollutants detected in greywater were screened for their potential to be transferred into the aquatic environment with the Estimation Programs Interface (EPI) Suite™ which was developed jointly by the US Environmental Protection Agency and Syracuse Research Corporation (SRC) (US EPA, 2012). Based on the EPI estimated value of the organic carbon-water partition coefficient (Koc) and the organic micro-pollutant partition coefficients (K_d) were calculated using equation 1.

$$K_d = Koc\ S_{oc} \qquad \text{equation 1}$$

where S_{oc} is the average soil organic carbon content of the site (Turner et al., 2013), note that two S_{oc} values were used, 2.9% at the soil surface (0 m) and 1.3% at depth (-0.3 m). These S_{oc} values are the average of values from the soil samples collected at the lot.

A K_d range was determined for the soil surface (0 m) and at depth (-0.3 m). Greywater micro-pollutants concentrations from the eight samples from the site were statistically summarised. The ratio of the estimated concentration of organic micro-pollutants bound to the soil compared to the dissolved concentration in the soil pore water at equilibrium was calculated using equation 2.

$$[OMP_b]{:}\,[OMP_s] = K_d\ \rho / Pw \qquad \text{equation 2}$$

where $[\mathrm{OMP_b}]$ is the concentration of organic micro-pollutant bound to the soil, $[\mathrm{OMP_s}]$ which is the concentration of organic micro-pollutant in solution, K_d is the organic micro-pollutant partition coefficient, ρ is the average soil bulk density of the studied lot (Turner et al., 2013) and Pw is the pore water volume based on water capacity in sandy clay loam of 15 to 32% and taking the highest capacity of 32% which is also the field capacity of sandy clay loam soils (Ley, 1994) resulting in Pw = 0.49 ml.

The final potential concentration of organic micro-pollutant in solution which could move to an aquatic environment was calculated for the surface soils then soils at -0.3 m using equation 3.

$$OMP_{soltn} = [\bar{x}GW]/([OMP_b]{:}\,[OMP_s] + 1) \qquad \text{equation 3}$$

where OMP_{soltn} is the estimated concentration of organic micro-pollutant in solution and available for transport to aquatic environments, $[\bar{x}GW]$ is the mean greywater concentration (µg L^{-1}) of the organic micro-pollutant and $[OMP_b]{:}\,[OMP_s]$ is the ratio of organic micro-pollutant bound to soil to that in solution at equilibrium. An average was then calculated for $[OMP_{con}]$ values for the surface soils and soils at -0.3 m depth.

3. Results and Discussion

Greywater

There were detections of 22 chemicals in the greywater sample (Table 1) out of the analysed 252 chemicals (Supplementary Information – organic micro-pollutant quality assurance and quality control). The chemicals that were detected included, pharmaceuticals, food additives/compounds, pesticides, fragrances and flame retardants. Some very hydrophilic (e.g., acesulfame) and very hydrophobic chemical (e.g., decachlorobiphenyl) chemicals with log Kow values ranging from -1.33 to 10.2 were detected. Table 1 gives examples of potential sources (household products) of the detected organic micro-pollutants in greywater. With such a wide range of detected chemicals from one household as well as the dynamic range of log Kow values it is easy to understand why organic micro-pollutants are classified as emerging compounds of concern. Furthermore the 22 detected chemicals could interact creating new chemicals and/or breakdown products that might be a potential hazard. Although greywater contains many organic micro-pollutants, land-based disposal through irrigation does provide a potential mechanism of binding and retaining many micro-pollutants, if managed correctly.

In general, the organic carbon content in surface soils is larger than subsurface soils, thus the K_d of surface soils will be larger than subsurface soils and surface soils will have a higher ability to bind organic micro-pollutants. Therefore, surface irrigation should pose a lower environmental risk due to the loss of organic micro-pollutants to aquatic environments via surface runoff or leaching to groundwater than subsurface irrigation. With this in mind, a key consideration in designing a greywater irrigation system would be to use sites with a low erosion risk i.e. grassed transpiration zones and determine whether greywater irrigation might be better applied to the surface than subsurface particularly in areas where there is the potential to interact with groundwater. Surface irrigation of greywater could however, increase the human health risks by increasing the potential for direct human contact.

210 **Table 1 The concentration of organic micro-pollutants detected in the one off screening greywater 24hr composite sample and a range of their physicochemical values.**

Micro-pollutant	Greywater concentration ($\mu g\ L^{-1}$)	Log Kow Log octanol-water partition coefficient (KOWWIN v1.68) [a]	Log Koc Soil adsorption coefficient (KOCWIN v2.00) [a]	Range of surface and subsurface soil K_d values	Molecular formula [a]	Potential household sources [b, c, d,e]
3,4-dichloroaniline	0.05	2.37	2.39	7.0–3.0	$C_6H_5Cl_2N_1$	herbicides, raw dye intermediates.
acesulfame	0.4	-1.33	0.340	0.06–0.03	$C_4H_5N_1O_4S_1$	artificial sweeteners
benzotriazole (1H-Benzotriazole, 5-methyl)	16	1.71	1.94	2.5–1.1	$C_7H_7N_3$	corrosion inhibitors for copper and drug precursors as an agonists for proteins
butylated hydroxytoluene (BHT - 2,6-Di-t-butyl-p-cresol)	1.8	5.10	3.91	235–106	$C_{15}H_{24}O_1$	antioxidant food additives.
caffeine	450	-0.07	0.98	0.28–0.12	$C_8H_{10}N_4O_2$	coffee
decachlorobiphenyl	96	10.2	5.64	12700–5700	$C_{12}Cl_{10}$	polychlorinated biphenyl (PCB) containing household products (e.g. dyes and pigments especially yellows) or chemical interaction by-products. Although PCB's were banned form production in 1979 according to USEPA they can still occur in a wide range of products e.g. oils, florescent bulbs, caulking, plastics, etc..
DEET (*N*,*N*-Diethyl-*meta*-toluamide)	1.5	2.18	1.85	2.0–0.9	$C_{12}H_{17}N_1O_1$	active ingredients in insect repellents
dibromobiphenyl	121	5.54	4.23	490–220	$C_{12}H_8Br_2$	flame retardants
diclofenac	0.01	4.51	2.60	11–5.2	$C_{14}H_{11}Cl_2NO_2$	nonsteroidal anti-inflammatory drugs (NSAID)
diuron	0.05	2.68	2.33	6–3	$C_9H_{10}Cl_2N_2O_1$	herbicides

galaxolide	24	5.90	4.09	360–160	$C_{18}H_{26}O_1$	musk used perfumes, soaps, cosmetics and detergents
ibuprofen	2.2	3.97	2.35	6.5–2.9	$C_{13}H_{18}O_2$	pain and fever reduction drugs
musk xylene (2-Nitro-m-xylen)e	36	2.25	3.58	110–49	$C_{12}H_{15}N_3O_6$	synthetic musk fragrances that mimic natural musk. These are used in perfumes and consumer products
paracetamol (acetaminophen)	0.09	0.46	1.32	0.61–0.27	$C_8H_9N_1O_2$	pain and fever reduction drugs
piperonyl butoxide	1	4.29	3.39	72–32	$C_{19}H_{30}O_5$	head lice shampoo treatments
propoxur	0.01	1.90	1.73	2.0–1.0	$C_{11}H_{15}N_1O_3$	flea and tick colour treatment and ant traps
pyrene-d10	120	4.88	4.23	490–220	$C_{16}D_{10}$	commercial dyes and dye precursors
salicylic acid	7.1	2.26	1.57	1.1–0.48	$C_7H_6O_3$	topical skin treatments, pain and fever reduction drugs, also anti-inflammatory drugs.
tonalid	1.5	5.70	4.27	540–240	$C_{18}H_{26}O_1$	fragrance used in detergent and fabric softeners
triclosan	21	4.76	3.92	240–110	$C_{12}H_7Cl_3O_2$	“antibacterial and antifungal agents found in consumer products, including soaps, detergents, toys
triphenyl phosphate	133	4.59	3.23	49–22	$C_{18}H_{15}O_4P_1$	plasticizer and flame fire retardants found in treated clothing.
tris(chloropropyl) phosphate isomers	1.5	3.11	2.75	16–7.3	$C_9H_{18}Cl_3O_4P_1$	flame retardants and plasticizers found in treated clothing.

[a]calculated using the Estimation Programs Interface (EPI) Suite™ v4.1 (US EPA 2012); [b] data from ChemSpider (2016); [c] data from Household product database (HPD 2016); [d] based on data http://www.thegoodscentscompany.com/index.html; [e] data from https://portal.apvma.gov.au/pubcris; (all data rounded to at least three significant figures).

Based on the initial screening for organic micro-pollutants, a smaller subset of six – acesulfame, caffeine, DDET, paracetamol, salicylic acid and triclosan – with log Kow values ranging from -1.33 to 4.76 (polar to nonpolar, Table 1) were used to determine if any of them were suitable markers of greywater contamination of aquatic environments. Caffeine and DEET were included as potential markers for greywater contamination as they have been widely identified as good molecular markers for wastewater contamination (Bruton et al., 2010; Aronson et al., 2012). However, caffeine can quickly biodegrade and can be produced from both natural and anthropogenic sources (McCance et al., 2018), nevertheless, this study detected markedly larger caffeine concentrations in the graywater compared to any other compound detected and thus would be a suitable marker of greywater contamination. Acesulfame was included as it was the most polar of the detected compounds, while paracetamol and salicylic acid were included as they had similar log Kow values as DEET and could therefore could also be good markers. Triclosan was included as it is one of the most non-polar compounds detected and to confirm that this compound is not mobile and not affecting the aquatic environment.

The results of the chemical analysis of greywater for the potential markers are summarised in Table 2. The potential markers were detected in every greywater sample (Table 2). The potential markers in order of descending maximum and mean concentrations in greywater, were: caffeine; triclosan; salicylic acid; DEET; acesulfame; and paracetamol.

Table 2 Concentration and frequency of detection of the organic micro-pollutants in greywater.

Compound	Detection frequency (%)	Concentrations in greywater of potential greywater markers (n=8)				
		Minimum (µg L^{-1})	Maximum (µg L^{-1})	Median (µg L^{-1})	Mean (µg L^{-1})	Standard deviation (µg L^{-1})
acesulfame	100	0.35	0.61	0.47	0.48	0.10
caffeine	100	240	1300	860	850	360
DEET	100	1.2	1.8	1.6	1.5	0.20
paracetamol	100	0.12	0.17	0.16	0.15	0.02
salicylic acid	100	2.4	4.8	3.8	3.6	1.0
triclosan	100	9.3	33	12	15	7.8

(data rounded to two significant figures).

Triclosan toxicity data published by Orvos et al. (2002) demonstrated the toxicity of triclosan to the algae *Scenedesmus subspicatus*, where 0.69 µg L^{-1} of triclosan was the "no observed effect concentration" (NOEC) and 1.4 µg L^{-1} of triclosan caused a 50% reduction in algae biomass (i.e. the EC50 biomass) after 96 hours exposure Thus, with minimum and maximum observed concentrations of triclosan of 9.3 µg L^{-1} and 33 µg L^{-1},

respectively. If triclosan ended up in the aquatic environment there is a high possibility of potential environmental harm. However, high concentrations of organic micro-pollutants will not necessarily result in larger concentrations in ground or surface water. This occurs because as the hydrophobicity of chemicals increases the concentration dissolved in the soil pore water decreases and soil pore water concentrations are directly related to the likely concentrations that will occur in groundwater and adjacent surface water. Estimated soil pore water concentrations of the potential markers of greywater decreased in the following order: caffeine; salicylic acid; acesulfame; DEET; paracetamol; and then triclosan. So even though triclosan had the second highest average concentration of organic micro-pollutants in greywater of 15 µg L^{-1} (Table 2) it was estimated that it would have the lowest soil pore water concentration of 0.03 µg L^{-1}(Table 3). Even before any dilution of soil pore water occurs on meeting groundwater aquifer or a surface waterway (e.g. Enoggera Creek) the concentrations would be well below the previously discussed EC50 and NOEC concentrations. Therefore, it is unlikely that triclosan will be a good marker for greywater contamination of the aquatic environment. It would, however, be a good marker for greywater contamination of soil. The fact that triclosan binds to soil in land based irrigation is an important concept, as literature notes that <60% of triclosan is removed from typical secondary waste water treatments plants.

Table 3 Organic micro-pollutants detected in greywater and their estimated soil pore-water characteristics.

Micro-pollutant	Log Koc soil adsorption coefficient (KOCWIN v2.00):	Mean concentration in greywater (µg L^{-1})	Ratio of chemical bound to soil and in solution $[OMP_b : OMP_s]$	Estimated average soil pore water solution concentration (µg L^{-1})
acesulfame	0.34	0.48	0.14	0.42
caffeine	0.98	850	0.59	550
DEET (*N*,*N*-Diethyl-*meta*-toluamide)	1.8	1.5	4.4	0.31
paracetamol (acetaminophen)	1.3	0.15	1.3	0.07
salicylic acid	1.6	3.6	2.3	1.2
triclosan	3.9	15	520	0.03

(data rounded to two significant figures).

Based on the average total organic carbon content of 2.9% in the surface soils and 1.3% in the subsurface soils (-0.3 m depth) of the lot there would be a decreased potential of the soil at depth to remove organic micro-pollutants (as the $[OMP_b]$: $[OMP_s]$ will decrease). For example, if the surface and subsurface soil were exposed to a solution with the same concentration of each of the selected potential markers, the ability of surface soil

to bind triclosan, DETT, salicylic acid, paracetamol, caffeine and acesulfame would be 55%, 47%, 42%, 35%, 25%, and 9% greater, respectively than the ability of the sub-surface to bind these chemicals. Further movement of organic micro-pollutants down through the soil profile, where the organic carbon content would likely decrease further, will result in an increased proportion of organic micro-pollutant in the soil pore-water as opposed to being bound to the soil. This increase risk with soil depth would apply to the majority of soil profiles where carbon content decreases the further you move down the profile, except vertisols, which have a thicker organic rich layer before decreasing with depth. If greywater is irrigated to soils with low organic matter content, the groundwater is more likely to be contaminated with organic micro-pollutants. The groundwater at this study site is especially at risk of organic micro-pollutant contamination as the aquifer is only 3 m below the surface, thus minimising the time for soil pore-water interaction to bind organic micro-pollutants.

Groundwater

There were no detections of paracetamol, salicylic acid or triclosan in the sampled groundwater while acesulfame, caffeine and DEET were detected in ≥90% of the groundwater samples (Table 4). The extent of dilution that the soil pore-water underwent in mixing with the groundwater was determined by dividing the estimated soil pore-water concentration for each micro-pollutant (Table 3) by the maximum measured concentration in groundwater or the PQL if a micro-pollutant was not detected. These resulted in dilution factors of <1 x for DEET, 1.2 x for acesulfame, 3.5 x for paracetamol, 6 x for triclosan, 240 x for salicylic acid and 3900 x for caffeine. There are two distinct groups of dilution factors those between 1 and 6 (i.e., acesulfame, paracetamol and triclosan) and those with markedly higher dilution factors of 240 and 3900 for salicylic acid and caffeine, respectively. Triclosan is an anti-microbial agent (Tamura et al., 2013) therefore it is unlikely that there was any degree of biodegradation during in the groundwater. Also half-lives of triclosan in soil range from 13 to 58 days (Ying et al., 2007; Wu et al., 2009; Xu et al., 2009) and in soils to which biosolids have been added of 73 to 301 days (Langdon et al., 2011). Given these characteristics of triclosan the dilution factors of 1 – 6 are a reasonable estimate of dilution due to the difference of volume of the pore-water and groundwater. It is therefore hypothesised that the markedly larger dilution factors of 240 and 3900 for salicylic acid and caffeine, respectively is caused by the removal of the vast majority of these two micro-pollutants by degradation processes. This is consistant with salicylic acid being readily consumed by microbial communities as a carbon source (US EPA., 2012). Only DEET had a dilution factor smaller than 1 (i.e., 0.02), indicating that

either DEET was concentrated in the groundwater which is very unlikely or that there was another source of DEET than the single residential lot investigated. As paracetamol, salicylic acid and triclosan were absent from groundwater it is highly unlikely they will be detected in the adjacent surface water.

Table 4 Summary statistics on the concentration and frequency of detection of the organic micro-pollutants in groundwater.

Compound	Detection frequency (%)	Concentration in groundwater (µg L^{-1}) of potential greywater markers (n=20)				
		Minimum	Maximum	Median	Mean	Standard deviation
acesulfame	90	0.003	0.340	0.066	0.090	0.098
caffeine	90	0.010	0.140	0.083	0.077	0.046
DEET	95	0.003	12	0.55	2.35	3.92
paracetamol	0	< PQL	< PQL	< PQL	< PQL	NC
salicylic acid	0	< PQL	< PQL	< PQL	< PQL	NC
triclosan	0	< PQL	< PQL	< PQL	< PQL	NC

NC = not calculable; < PQL = less than practical quantitation level. (data rounded to at least three significant figures).

Surface water

The three micro-pollutants detected in the groundwater (acesulfame, caffeine and DEET) were all detected at the impact site in Enoggera Creek (Table 5). In addition, salicylic acid was also detected at the impact site, albeit at a low detection frequency of 17% (Table 5). The same four organic micro-pollutants were also detected at the control site (upstream of potential greywater contamination) but at a lower detection frequency and lower mean concentrations (Table 5) than at the impact site, except acesulfame which had a higher mean concentration. These results suggest that greywater is not the only source of these chemicals. Samples from the reference site (Enoggera Reservoir) contained only DEET and this occurred at similar mean concentrations to the control site (0.011 and 0.012 µg L^{-1}, respectively) but less frequently (58% and 67%, respectively) (Table 5). The reference site is located in a high ecological value area (EHP 2010) and in theory has no or minimal diffuse pollutant sources and yet DEET was regularly detected (Table 5). This finding is contradictory to the US EPA DEET RED Fact Sheet (US EPA, 1998) available on the US EPA website (US EPA, 2016) that states that DEET was not an aquatic compound of concern as it is not directly used in the environment. Rather, the results from this study support research by Costanzo et al. (2007) and Weeks et al. (2010) that indicates that contamination by DEET might be ubiquitous in the aquatic environment.. However, DEET was detected more frequently (Table 5) and at significantly higher concentrations at the impact site than both the control (p = 0.014,) and reference sites (p = 0.011), indicating that greywater is a source of DEET to Enoggera Creek (Table 6).

Salicylic acid was detected at a similar frequency and not significantly different concentrations at both the control and impact sites in Enoggera Creek (Table 6) indicating that its source is not greywater but the source occurs between the reservoir wall and the control site. This is possible as there are a small number of houses located between the reservoir wall and the control site. While these do not have formal greywater irrigation systems they could be manually irrigating their greywater as this is often practiced in Brisbane (BCC, 2016).

In contrast, while caffeine was detected at both the control and impact sites (Table 5), detections were more frequent and at significantly higher concentrations at the impact site (p = 0.005, Table 6). Therefore, indicating that greywater is a source of these chemicals to Enoggera Creek.

Acesulfame was also detected at both the control and impact sites. However, while acesulfame was detected more frequently at the impact site (Table 5) the concentrations were not significantly different (p = 0.953). Thus, there is no evidence that irrigated greywater is a source of acesulfame to Enoggera Creek. Box and whisker plots showing the variation of concentrations at the impact, control and reference sites for each of the organic micro-pollutants are available in Supplementary Information – organic micro-pollutants in surface water.

Table 5 Summary statistics of frequency of detection and the concentration of organic micro-pollutants detected in Enoggera Creek (control and impact sites) and Enoggera Reservoir (reference site).

Surface water site	Compound	Detection frequency (%)	Minimum (µg L^{-1})	Maximum (µg L^{-1})	Median (µg L^{-1})	Mean (µg L^{-1})	Standard deviation (µg L^{-1})
Impact (n = 28)	acesulfame	83	0.003	0.060	0.018	0.018	0.013
	caffeine	67	0.010	0.110	0.020	0.034	0.029
	DEET	83	0.003	0.110	0.022	0.032	0.030
	paracetamol	nd	< PQL	< PQL	< PQL	< PQL	nc
	salicylic acid	17	0.003	0.200	0.003	0.026	0.056
	triclosan	nd	< PQL	< PQL	< PQL	< PQL	nc
Control (n = 26)	acesulfame	71	0.003	0.090	0.010	0.025	0.030
	caffeine	38	0.007	0.110	0.010	0.025	0.030
	DEET	67	0.003	0.030	0.012	0.012	0.008
	paracetamol	nd	< PQL	< PQL	< PQL	< PQL	nc
	salicylic acid	8	0.003	0.500	0.003	0.025	0.099
	triclosan	nd	< PQL	< PQL	< PQL	< PQL	nc
Reference (n = 12)	acesulfame	nd	< PQL	< PQL	< PQL	< PQL	nc
	caffeine	nd	< PQL	< PQL	< PQL	< PQL	nc
	DEET	58	0.003	0.022	0.011	0.010	0.007
	paracetamol	nd	< PQL	< PQL	< PQL	< PQL	nc
	salicylic acid	nd	< PQL	< PQL	< PQL	< PQL	nc
	triclosan	nd	< PQL	< PQL	< PQL	< PQL	nc

nd = not detected; nc = not calculable; < PQL = less than practical quantitation level (data rounded to three significant figures).

Table 6 Probabilities that significant differences occurs between the concentrations of acesulfame caffeine, DEET and salicylic acid present at the reference (R), control (C) and impact (I) sites. Probabilities are from Bonferroni analysis of the differences.

	acesulfame	caffeine	DEET	salicylic acid
R vs I	**< 0.0001**	**0.0004**	**0.011**	0.149
R vs C	**< 0.0001**	0.182	0.588	0.403
C vs I	0.953	**0.005**	**0.014**	0.451

To confirm that caffeine and DEET in the groundwater are in fact influencing the surface water, plots of their concentrations in groundwater and the impact site in Enoggera Creek over time were generated (Figure 2 and Figure 3). In general, the temporal variation in their concentrations are very similar, but with the surface water showing more short term changes reflecting the greater influence of rainfall on its concentrations. These plots and the earlier analysis provide strong evidence that the groundwater and surface water in Enoggera Creek are directly connected and that groundwater directly influences the chemistry of the water at the impact site and potentially further downstream. Unfortunately, the temporal resolution of the groundwater sampling does not allow for the calculation of advection coefficients to determine possible organic micro-pollutant travel times. However based on Figure 2 and Figure 3 the organic micro-pollutant appears to move ~98 m from the groundwater sampling sites (piezometers) to the surface water impact site within a 24 to 72 hr period. This indicates a groundwater flow rate of between 32 to 98 m day^{-1}, which is considerably higher than the estimated hydraulic conductivity of 2.7 m day^{-1} (AGE, 2006) and 3.6 m day^{-1} (SKM-aurecon, 2011), for the same region. The high hydraulic conductivities estimated in this project, compared to those estimated previously for the same region, could be due to the steep slope of the subdivision (i.e., up to 20%, Turner et al., 2016) With the strong statistical information that caffeine and DEET will be good molecular markers for greywater contaminating the aquatic environment and with this clear link of greywater contaminating the surface water, it is now possible to assess the contamination of other greywater constituents which have natural environmental concentrations (i.e. cations, anions, nutrients and metals) and are observed at the impact site. Although these organic micro-pollutants appear to be at very low concentration research by Turner et al. (2013 and 2016) highlighted that there was potential contamination in the soil, in the groundwater and surface waters from other chemicals including nutrients, major cations and anions as well as metals and metalloids. Loads (the total amount) for other greywater constituents (i.e. cations, anions, nutrients and metals) observed

at the impact site could also be calculated. By calculating the load at the impact site and by calculating the annual load for irrigated greywater we can assess the total amount (load) being contributed from greywater irrigation to the local creek. This requires further analysis and then assessment of the associated impacts.

4. Conclusions

Chemical analysis of greywater detected the presence of 22 organic micro-pollutants. Six of these organic micro-pollutants (acesulfame, caffeine, DEET, paracetamol, salicylic acid and triclosan) were selected to test their suitability as tracers of greywater. Only acesulfame, caffeine and DEET were detected in groundwater while in an adjacent surface waterway salicylic acid was also detected but only caffeine and DEET were directly attributable to greywater. This study clearly shows that the practice of sub-surface irrigation of greywater can lead to contamination of shallow groundwater and adjacent surface waters by organic micro-pollutants. The full potential of irrigated greywater as a source of micro-pollutants to groundwater and adjacent surface water and the risk this poses requires further analysis. It is likely that surface irrigation of greywater would reduce the risk posed, by binding a greater proportion of micro-pollutants to soil, however this must be balanced with an increased risk of exposure to humans.

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Figures

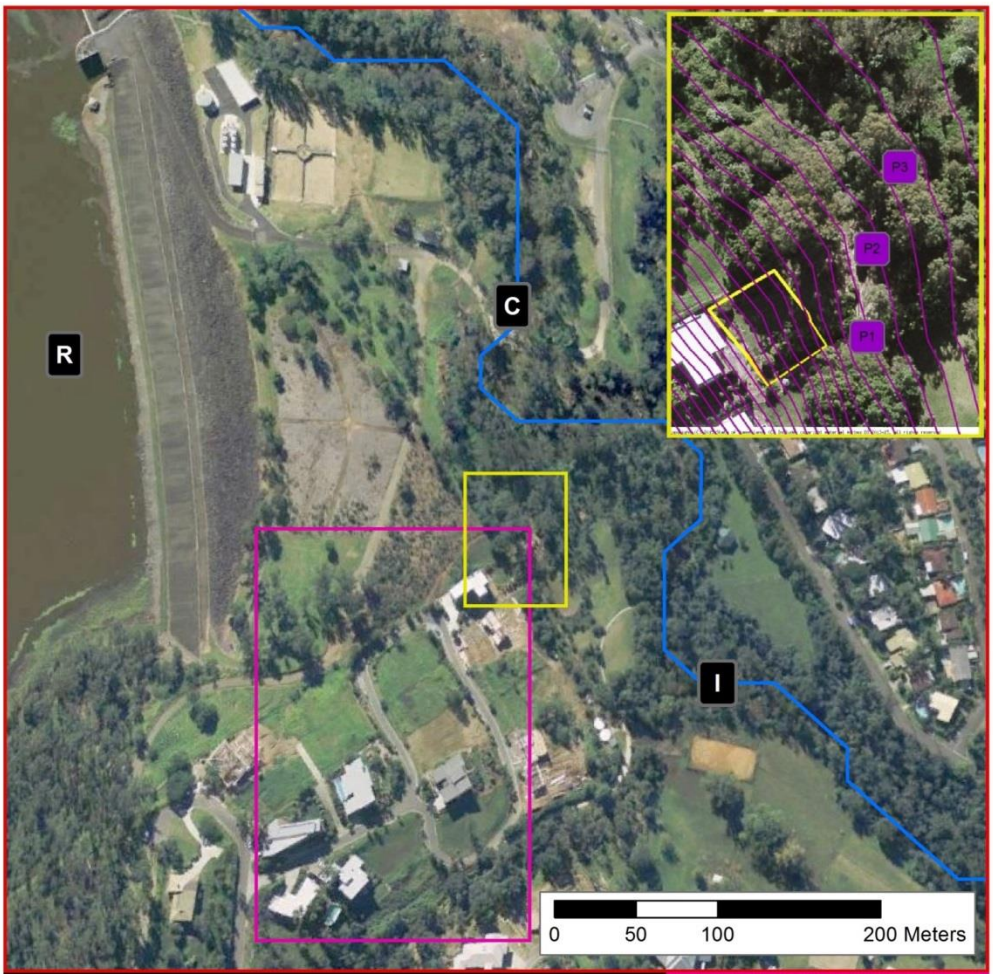
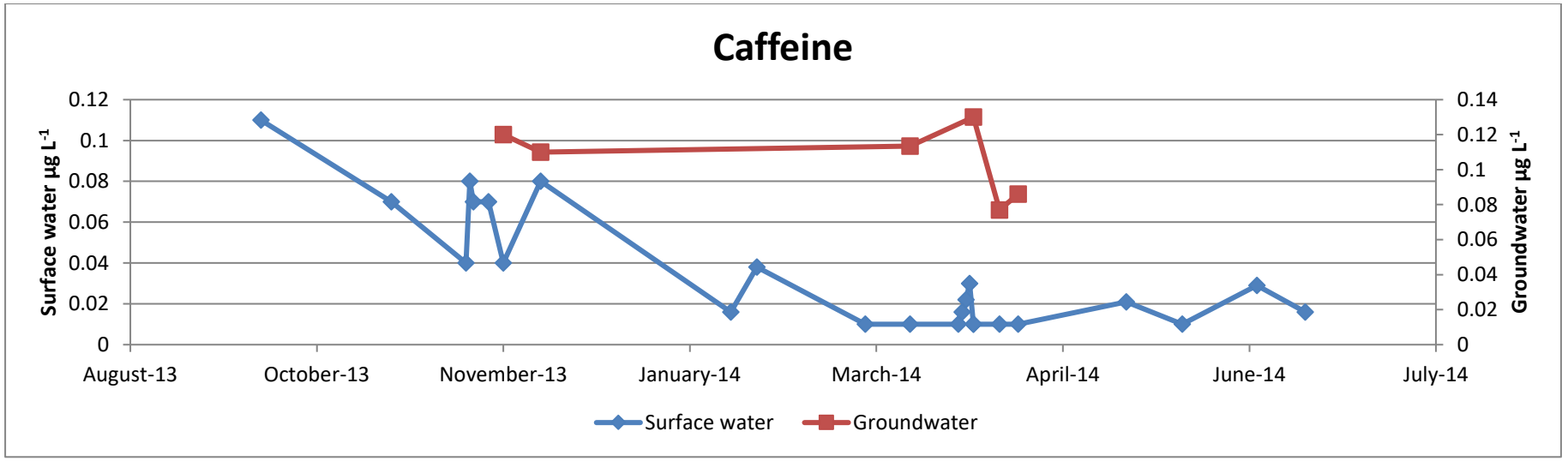


Figure 1 Study site location, aerial photograph (red box); study site (purple box) and Enoggera Creek location (blue line) with the surface water sampling sites marked (black boxes); reference site (R) in Enoggera Reservoir, upstream control (C) site and downstream impact (I) site. Zoom 2 (yellow box); indicates the general topography (pink contours) and lot D with the location of its transpiration zone (yellow outline) and the piezometers (purple squares numbered P1 to P3). (Aerial photograph: Copyright © 2015 State of Queensland includes Copyright © Airbus DS 2013-15).



513
514 Figure 2 Groundwater and surface water caffeine concentrations over time
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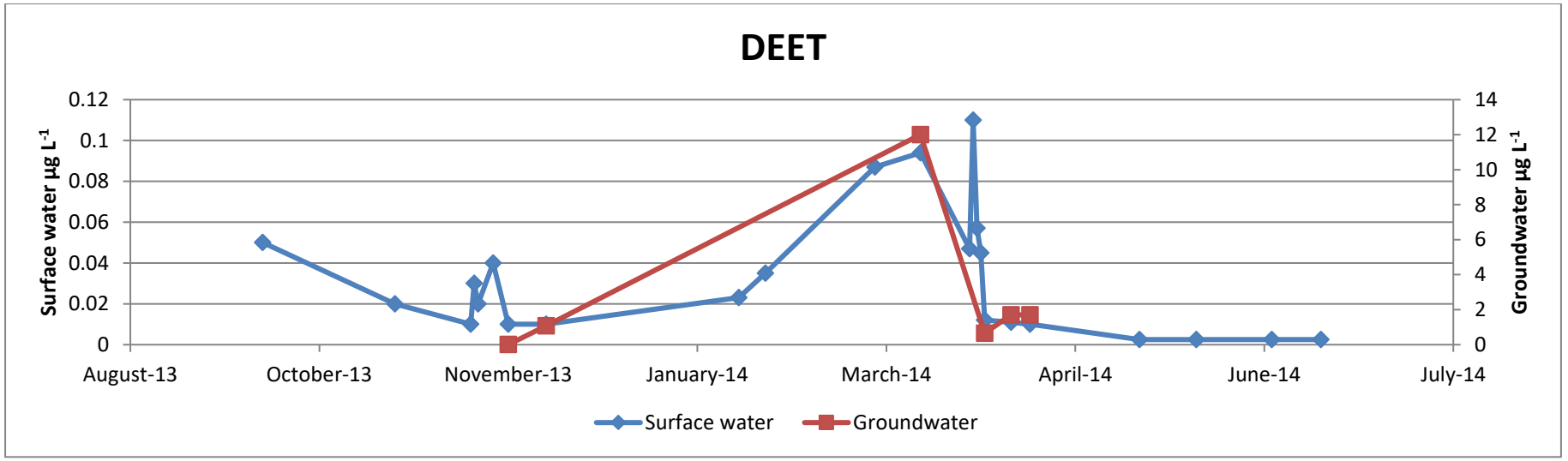

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517 Figure 3 Groundwater and surface water DEET concentrations over time